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(54) **Condensation curable silicone foul release coatings and articles coated therewith**

RTV-bewuchshemmende Silikon-Beschichtungen und damit beschichtete Gegenstände

Revêtement antisalissure de RTV-silicone et articles ainsi revêtus

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Description

[0001] This invention relates to foul release coatings and articles coated therewith.

[0002] As poetically stated in US Patent 4,861,670, "Marine fouling due to pernicious and pestiferous sessile organisms is a problem which reaches from ancient times to the present." In more simple terms, a perennial major aggravation to shippers and users of marine equipment in contact with water is the tendency of such equipment to become encrusted with varieties of wildlife, as illustrated by barnacles and zebra mussels.

[0003] Said patent goes on to describe in considerable detail the types of treatments that have been employed, starting as early as 1854, to minimize marine fouling. Treatment materials have included compounds of such metals as copper, tin, arsenic, mercury, zinc, lead, antimony, silver and iron, as well as toxic organic materials such as strychnine and atropine. With increasing interest in the state of the environment, the use of such materials has been strongly discouraged.

[0004] More recently, polyorganosiloxanes (hereinafter sometimes designated "silicones" for brevity) have been found useful as anti-fouling coatings. They include condensation cured room temperature vulcanizable (hereinafter sometimes "RTV") compositions comprising silica as a filler in combination with silanol - or trialkoxy-terminated siloxanes, catalysts and crosslinking agents. They may be made sprayable by dilution with solvents, typically volatile organic compounds such as hydrocarbons.

[0005] US-A-5218059 discloses non toxic anti-fouling coating compositions comprising 50-99% by weight of a reaction curable silicone resin having a hydroxyl or alkoxy group directly bonded to a terminal silicon atom and 1-50% by weight of a silicone resin having an alkoxy group bonded to silicon directly or through an ether, ester or NH group.

[0006] There is still a need, however, to improve various properties of RTV-based foul release coatings, particularly their release efficiency and their effective lifetime.

SUMMARY OF THE INVENTION

[0007] The present invention is based on the discovery that addition of specifically defined water-insoluble silicones to a conventional RTV formulation improves foul release properties. It includes foul release coatings having said improved properties and articles coated therewith.

[0008] In one of its aspects, the invention is directed to condensation curable coating compositions comprising the following and any reaction products thereof:

(A) a one- or two-part room temperature vulcanizable polyorganosiloxane composition, and

(B) a marine foul release-enhancing proportion of at least one polyorganosiloxane free from silanol groups and comprising about 10-60% by weight of at least one hydroxy- terminated polyoxyalkylenealkyl radical,

[0009] Component B is capable of blooming to the surface of the cured product of component A.

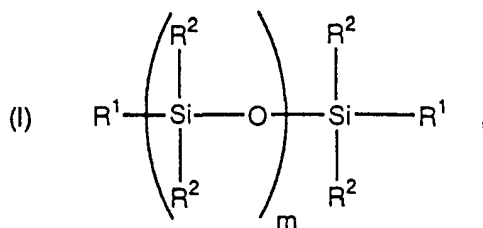
[0010] Another aspect of the invention is articles comprising a marine structure coated with an anti-fouling coating which is the condensation cured reaction product of the composition defined hereinabove.

DETAILED DESCRIPTION; PREFERRED EMBODIMENTS

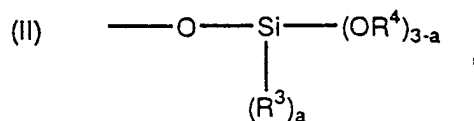
[0011] The word "component" is frequently employed herein for brevity to designate the materials present in the compositions of the invention. Its use is independent of the possible interreaction of said materials to form other chemical constituents.

[0012] Component A of the compositions of the invention may be a conventional one-part or two-part RTV composition; it is most often a two-part composition. It typically comprises at least one reactive silicone, at least one condensation catalyst and at least one crosslinking agent.

[0013] The reactive silicone is most often a polydialkylsiloxane, typically of the formula



wherein each R¹ is hydroxyl or



each R² is independently a hydrocarbon or fluorinated hydrocarbon radical, each R³ and R⁴ is a hydrocarbon radical, a is 0 or 1 and m has a value such that the viscosity of said reactive silicone under ambient temperature and pressure conditions is up to about 50,000 centipoise. Illustrative hydrocarbon radicals are C₁₋₂₀ alkyl, C₆₋₂₀ aryl and alkaryl, vinyl, isopropenyl, allyl, butenyl and hexenyl, with C₁₋₄ alkyl and especially methyl being preferred. An illustrative fluorinated hydrocarbon radical is 3,3,3-trifluoropropyl. Most often, each R², R³ and R⁴ is alkyl and preferably methyl.

[0014] It is within the scope of the invention to employ two or more reactive silicones, differing in average molecular weight. This may afford a bimodal composition having performance advantages over a simple monomodal composition.

[0015] The condensation catalyst may be any of those known to be useful for promoting condensation curing of an RTV material. Suitable catalysts include tin, zirconium and titanium compounds as illustrated by dibutyltin dilaurate, dibutyltin diacetate, dibutyltin methoxide, dibutyltin bis(acetylacetonate), 1,3-dioxopropanetitanium bis(acetylacetonate), titanium naphthenate tetrabutyl titanate and zirconium octanoate. Various salts of organic acids with such metals as lead, iron, cobalt, manganese, zinc, antimony and bismuth may also be employed, as may non-metallic catalysts such as hexylammonium acetate and benzyltrimethylammonium acetate. For most purposes, the tin and titanium compounds are preferred.

[0016] As crosslinking agents, trifunctional (T) and tetrafunctional (Q) silanes are useful, the term "functional" in this context denoting the presence of a silicon-oxygen bond. They include such compounds as methyltrimethoxysilane, methyltriethoxysilane, 2-cyanoethyltrimethoxysilane, methyltriacetoxysilane, tetraethyl silicate and tetra-n-propyl silicate. The Q-functional compounds, i.e., tetraalkyl silicates, are often preferred.

[0017] Component A may contain other constituents, including reinforcing and extending (non-reinforcing) fillers. Typical reinforcing fillers are commercially available in the form of relatively large aggregated particles, typically having an average size significantly greater than 300 nm. The preferred fillers are the silica fillers, including fumed silica and precipitated silica. These two forms of silica have surface areas in the ranges of 90-325 and 80-150 m²/g, respectively.

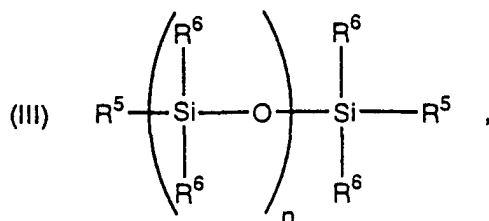
[0018] The reinforcing filler is most often pretreated with a treating agent to render it hydrophobic. Typical treating agents include cyclic silicones such as cyclooctamethyltetrasiloxane and acyclic and cyclic organosilazanes such as hexamethyldisilazane, 1,3-divinyl-1,1,3,3-tetramethyldisilazane, hexamethylcyclotrisilazane, octamethylcyclotetrasilazane and mixtures of these. Hexamethyldisilazane is often preferred.

[0019] Non-reinforcing fillers include titanium dioxide, lithopone, zinc oxide, zirconium silicate, iron oxides, diatomaceous earth, calcium carbonate, glass fibers or spheres, magnesium oxide, chromic oxide, zirconium oxide, aluminum oxide, crushed quartz, calcined clay, talc, kaolin, asbestos, carbon, graphite, cork, cotton and synthetic fibers.

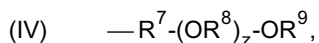
[0020] The proportions of the constituents of component A may be varied widely. The amount of filler is generally about 5-200 parts and preferably about 10-150 parts by weight per 100 parts of reactive silicone. Catalysts and crosslinkers are generally present in the amounts of about 0.001-2.5% and about 0.25-5.0% by weight respectively, based on the combination of reactive silicone and filler.

[0021] Component B is a water-insoluble polyorganosiloxane free from silanol groups and containing at least one hydroxy- or alkoxy-terminated polyoxyalkylenealkyl radical. Said radical or radicals comprise about 10-60% by weight of component B; that is, the molecular weight attributable to said radicals is about 10-60% by weight of the total molecular weight attributable to component B.

[0022] In general, component B comprises compounds of the formula



wherein each R⁵ is a hydrocarbon radical and each R⁶ is a hydrocarbon or fluorinated hydrocarbon radical, with the proviso that at least one of the R⁵⁻⁶ radicals has the formula



wherein R⁷ and each R⁸ is independently C₂₋₆ alkylene and R⁹ is hydrogen; n has a value such that the weight average molecular weight of the compound of formula III is in the range of about 500-40,000; and z and the number of radicals of formula IV are such that said radicals of formula IV comprise about 10-60% by weight of component B. The illustrative and preferred hydrocarbon radicals for R⁵⁻⁶ are the same as those for R¹⁻². R⁷ and R⁸ may be, for example, ethylene, propylene or trimethylene; R⁷ is preferably trimethylene and R⁸ is preferably ethylene. R⁹ is most often hydrogen or methyl.

[0023] Illustrative compounds of formula III are available from Gelest, Inc., under the trade designations "DMS-C" and "DBE". One illustration of such a compound is "DMS-C15" which has a molecular weight of 1,000 and a viscosity in the range of 30-50 mPa.s (centipoise) and in which each R⁶ is methyl, each R⁵ has formula IV, R⁷ is trimethylene, R⁸ is ethylene, R⁹ is hydrogen and the radicals of formula IV constitute about 20% by weight of the molecule. More generally, the compounds employed as component B which contain internal radicals of formula IV should contain them in an amount to provide about 20-30% by weight of the molecule.

[0024] Component B is present in the compositions of the invention in an effective proportion to enhance foul release properties. For the most part, about 5-20 parts by weight per 100 parts of component A is adequate. The essential property of component B is that of blooming to the surface of the cured product of component A during or after the curing process, by reason of its higher polarity than component A.

[0025] The compositions of this invention may also incorporate further constituents such as non-reactive silicone oils, dyes, solubilizing agents and solvents to render them sprayable if sprayability is desirable. These may be introduced as part of component A or as adjuvants to the entire composition, as appropriate.

[0026] Suitable solvents include aromatic hydrocarbons such as toluene or xylene and aliphatic hydrocarbons such as petroleum naphtha. Solubilizing agents include vinyl-substituted silicones, generally present, if at all, in amounts up to about 25% by weight based on the combination of components A and B.

[0027] The marine structures in the articles of the invention are often ships' hulls. However, other underwater articles such as liquid collecting and discharge pipes, dry dock equipment and the like are included. Suitable materials therefor include metals such as iron and aluminum and resinous materials such as fiber-reinforced thermoplastic or thermoset resins.

[0028] Application of the compositions of the invention is typically preceded by the application of conventional pre-treatment layers. These may include, for example, anti-corrosive epoxy primers, mist coats and tie-layers comprising polyorganosiloxanes and toughening components. The compositions of the invention may be applied by conventional techniques such as brushing or drawing down, or by spraying if they are suitably diluted.

[0029] The invention is illustrated by the following examples. All parts and percentages are by weight.

EXAMPLE 1

[0030] A condensation curable RTV composition was prepared by blending the following constituents in the amounts indicated:

Part I:

Silanol-stopped polydimethylsiloxane, viscosity 30,000 mPas. (centipoise)- 100 parts;

non-reactive polydimethylsiloxane oil, viscosity 20 mPas (centipoise)- 38.5 parts;

n-propyl silicate - 12.13 parts;

fumed silica, hexamethyldisilazane-treated - 37 parts.

Part II: dibutyltin dilaurate.

[0031] The two parts, also containing conventional additives such as non-reinforcing fillers, dyes and compatibilizers, were combined in proportions such that the dibutyltin dilaurate was present in the amount of 2.43 parts per 100 parts of silanol-stopped polydimethylsiloxane. To the resulting RTV composition was added 10% by weight, based on RTV

composition, of a polydimethylsiloxane having hydroxy-terminated 3-(polyoxyethylene)propyl end groups and a weight average molecular weight of about 1,000(DMS-C15). The composition thus prepared was applied by curtain coating to aluminum test panels which had been previously coated with a commercially available epoxy anti-corrosion coating, mist coat and tie-layer. The test panels were exposed to water for 12 months, after which time 91-99% of their surface area was unfouled and no encrusting bryozoans were present. A control panel, coated with the RTV composition alone, had 66-69% of its surface area unfouled and had 25-50% encrusting bryozoans.

EXAMPLES 2-3

[0032] An RTV composition was prepared by blending (Part I) 70 parts of a silanol-terminated polydimethylsiloxane having a viscosity of 3,100 mPas (centipoise) 90 parts of calcium carbonate and 2 parts of tetraethyl silicate, and (Part II) 0.5 part of dibutyltin dilaurate. There were then added 10%, based on RTV composition, of the following

[0033] Example 2 - the hydroxy-terminated 3-(polyoxyethylene)propyl polydimethylsiloxane of Example 1.

[0034] Example 3 - a methyl-terminated polydimethylsiloxane containing internal methoxy-terminated 3-(polyoxyethylene)propyl groups and having a weight average molecular weight of 10,000.

[0035] Aluminum test panels similar to those of Example 1 were primed with a commercially available primer and then curtain coated with the compositions of Examples 2-3. They were then submerged in a salt water lagoon in Florida in cages until barnacle settlement occurred. At the end of the test period, barnacle adhesion, as determined by ASTM test procedure D5618, for the panels coated with the products of Examples 2 and 3 were 4.76 and 35.71 kPa (0.69 and 5.18 psi), respectively. A control panel coated with the RTV composition only had a barnacle adhesion of 71.36 kPa (10.35 psi).

Claims

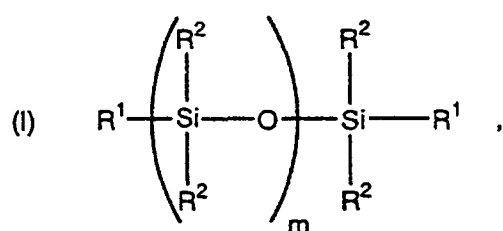
1. A condensation curable coating composition comprising the following and any reaction products thereof:

(A) a one- or two-part room temperature vulcanizable polyorganosiloxane composition, and

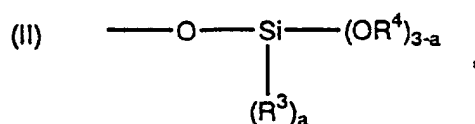
(B) a marine foul release-enhancing proportion of at least one polyorganosiloxane free from silanol groups and comprising about 10-60% by weight of at least one hydroxy terminated polyoxyalkylenealkyl radical.

2. A composition according to claim 1 wherein component A comprises at least one reactive silicone, at least one condensation catalyst and at least one crosslinking agent.

3. A composition according to claim 2 wherein the reactive silicone is a polydialkylsiloxane having the formula

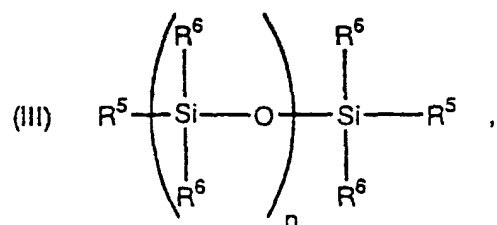


wherein each R^1 is hydroxyl or

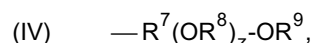


each R^2 is independently a hydrocarbon or fluorinated hydrocarbon radical, each R^3 and R^4 is a hydrocarbon radical, a is 0 or 1 and m has a value such that the viscosity of said reactive silicone under ambient temperature and pressure conditions is up to about 50,000 mPas (centipoise.)

4. A composition according to claim 2 wherein the condensation catalyst is a tin, zirconium or titanium compound.
5. A composition according to claim 2 wherein the crosslinking agent is a trifunctional or tetrafunctional silane.
6. A composition according to any preceding claim wherein component B comprises compounds of the formula



wherein each R^5 is a hydrocarbon radical and each R^6 is a hydrocarbon or fluorinated hydrocarbon radical, with the proviso that at least one of the R^{5-6} radicals has the formula

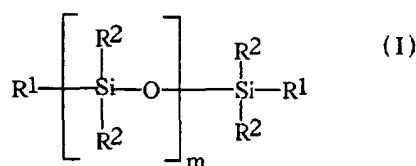


wherein R^7 and each R^8 is independently C_{2-6} alkylene and R^9 is hydrogen; n has a value such that the weight average molecular weight of the compound of formula III is in the range of about 500-40,000; and z and the number of radicals of formula IV are such that said radicals of formula IV comprise about 10-60% by weight of component B.

7. A composition according to claim 6 wherein each R^5 and R^6 that does not have formula IV is methyl.
8. A composition according to claim 6 wherein component B has a viscosity in the range of 30-50 mPas (centipoise) and each R^6 therein is methyl, each R^5 has formula IV, R^7 is trimethylene, R^8 is ethylene and R^9 is hydrogen.
9. An article comprising a marine structure coated with an anti-fouling coating which is the condensation cured reaction product of a condensation curable coating composition according to any preceding claim.

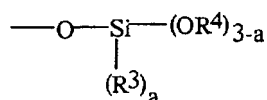
Patentansprüche

1. Kondensations-härtbare Überzugs-Zusammensetzung, umfassend das Folgende und irgendwelche Reaktionsprodukte davon:
- (A) eine bei Raumtemperatur vulkanisierbare Einkomponenten- oder Zweikomponenten-Polyorganosiloxan-Zusammensetzung und
- (B) einen Meerwasser-Verschmutzung freisetzenden Anteil mindestens eines Polyorganosiloxans ohne Silanolgruppen, umfassend etwa 10-60 Gew.-% mindestens eines Hydroxy-Endgruppen aufweisenden Polyoxalkylenalkylrestes.
2. Zusammensetzung nach Anspruch 1, worin Komponente (A) mindestens ein reaktives Silicon, mindestens einen Kondensations-Katalysator und mindestens ein Vernetzungsmittel umfasst.
3. Zusammensetzung nach Anspruch 2, worin das reaktive Silicon ein Polydialkylsiloxan der Formel ist



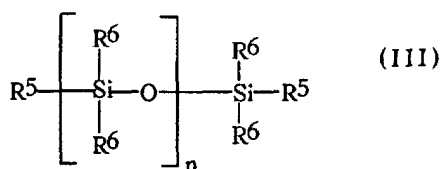
worin jedes R^1 Hydroxyl oder

(II)

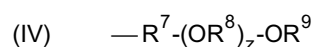


ist, jedes R^2 unabhängig ein Kohlenwasserstoff- oder fluorierter Kohlenwasserstoffrest ist, jedes R^3 und R^4 ein Kohlenwasserstoffrest ist, a null oder 1 ist und m einen solchen Wert hat, dass die Viskosität des reaktiven Silicons bei Umgebungs-Temperatur- und -Druckbedingungen bis zu 50.000 mPa·s (centipoise) beträgt.

4. Zusammensetzung nach Anspruch 2, worin der Kondensations-Katalysator eine Zinn-, Zirkonium- oder Titan-Verbindung ist.
5. Zusammensetzung nach Anspruch 2, worin das Vernetzungsmittel ein trifunktionelles oder tetrafunktionelles Silan ist.
6. Zusammensetzung nach einem vorhergehenden Anspruch, worin Komponente B Verbindungen der Formel umfasst



worin jedes R^5 ein Kohlenwasserstoffrest und jedes R^6 ein Kohlenwasserstoff- oder fluorierter Kohlenwasserstoffrest ist, unter der Bedingung, dass mindestens einer der R^{5-6} -Reste die Formel hat



worin R^7 und jedes R^8 unabhängig C_{2-6} -Alkylen und R^9 Wasserstoff ist, n einen solchen Wert hat, dass das Gewichtsmittel des Molekulargewichtes der Verbindung der Formel III im Bereich von etwa 500-40.000 liegt und z und die Anzahl der Reste der Formel IV derart sind, dass die Reste der Formel IV etwa 10-60 Gew.-% der Komponente B umfassen.

7. Zusammensetzung nach Anspruch 6, worin jedes R^5 und R^6 , das nicht Formel IV aufweist, Methyl ist.
8. Zusammensetzung nach Anspruch 6, worin Komponente B eine Viskosität im Bereich von 30-50 mPa·s (centipoise) hat und jedes R^6 darin Methyl ist, jedes R^5 Formel IV hat, R^7 Trimethylen ist, R^8 Ethylen ist und R^9 Wasserstoff ist.
9. Gegenstand, umfassend eine Schiffsstruktur, die mit einem der Verschmutzung entgegenwirkenden Überzug überzogen ist, der ein kondensations-gehärtetes Reaktionsprodukt einer kondensations-härtbaren Überzugszusammensetzung nach einem vorhergehenden Anspruch ist.

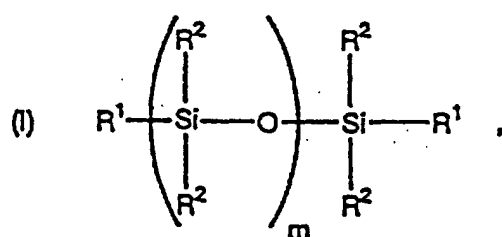
Revendications

1. Composition de revêtement durcissable par condensation, comprenant les composés suivants et leurs produits réactionnels :

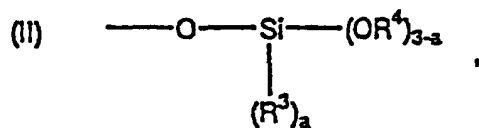
(A) une composition de polyorganosiloxane vulcanisable à température ambiante, à un ou deux composants, et
 (B) une proportion renforçant l'élimination des salissures marines, d'au moins un polyorganosiloxane exempt de groupes silanols et comprenant environ 10 à 60 % en poids d'au moins un groupe polyoxyalkylènealkyle à terminaison hydroxy.

2. Composition selon la revendication 1, dans laquelle le composant A comprenant au moins une silicone réactive, au moins un catalyseur de condensation et au moins un agent de réticulation.

3. Composition selon la revendication 2, dans laquelle la silicone réactive est un polydialkylsiloxane répondant à la formule :

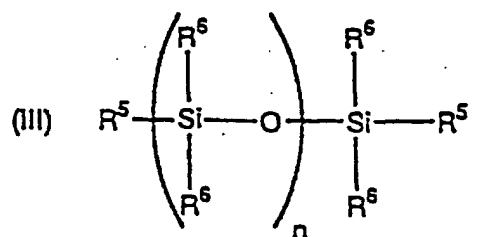


dans laquelle chaque R^1 représente un groupe hydroxy ou

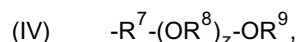


chaque R^2 représente indépendamment un groupe hydrocarboné ou un groupe hydrocarboné fluoré, chaque R^3 et chaque R^4 représentent un groupe hydrocarboné, a vaut 0 ou 1 et m a une valeur telle que la viscosité de ladite silicone réactive dans des conditions de température et de pression ambiantes va jusqu'à environ 50 000 mPa.s (centiPoise).

4. Composition selon la revendication 2, dans laquelle le catalyseur de condensation est un composé d'étain, de zirconium ou de titane.
5. Composition selon la revendication 2, dans laquelle l'agent de réticulation est un silane trifonctionnel ou tétrafonctionnel.
6. Composition selon l'une quelconque des revendications précédentes, dans laquelle le composant B comprend des composés de formule :



dans laquelle chaque R^5 représente un groupe hydrocarboné et chaque R^6 représente un groupe hydrocarboné ou un groupe hydrocarboné fluoré, sous réserve qu'au moins l'un des groupes R^5 et R^6 répondent à la formule :



dans laquelle R^7 et chaque R^8 représentent indépendamment un groupe alkylène en C_{2-6} et R^9 représente un atome d'hydrogène ; n a une valeur telle que la masse moléculaire moyenne en poids du composé de formule III se situe dans l'intervalle allant d'environ 500 à 40 000 ; et z et le nombre de groupes de formule IV sont tels que lesdits groupes de formule IV représentent environ 10 à 60 % en poids du composant B.

7. Composition selon la revendication 6, dans laquelle chaque R^5 et chaque R^6 qui ne répondent pas la formule IV, représentent un groupe méthyle.
8. Composition selon la revendication 6, dans laquelle le composant B présente une viscosité se situant dans l'intervalle allant de 30 à 50 mPa.s (centipoise) et chaque R^6 représente un groupe méthyle, chaque R^5 répond à la formule IV, R^7 représente un groupe triméthylène, R^8 représente un groupe éthylène et R^9 représente un atome d'hydrogène.
9. Article comprenant une structure marine revêtue d'un revêtement anti-salissure qui est le produit réactionnel durci par condensation d'une composition de revêtement durcissable par condensation selon l'une quelconque des revendications précédentes.